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The Hexagonal Structure II of Clathrate Hydrate $Me_4NF \cdot 0.5Pr_4NF \cdot 15H_2O$

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The phase diagram of the tetramethylammonium fluoride–tetrapropylammonium fluoride–water system has been studied in the crystallization field; hydrate $Me_4NF \cdot 0.5Pr_4NF \cdot 15H_2O$ (m.p. 21.7 °C) with hexagonal II unit cell: a = 12.290 Å, c = 59.354 Å has been discovered and so, as predicted by Jeffrey, the hexagonal structure II framework has been confirmed experimentally.

In spite of the fact that clathrate hydrates most frequently crystallize to form cubic structure II (CS-II), hexagonal structure II (HS-II) with the same ratio of the same kind of H and D cavities has never been observed. HS-II differs from CS-II in the manner in which the layers consisting of pentagonal dodecahedra *abcabc* in HS-II and *abab* in CS-II alternate.[1] The stoichiometry of the idealized water frameworks of these two structures can be illustrated by the formula $H \cdot 2D \cdot 17H_2O$ (H and D are the cavities $5^{12}6^4$ and 5^{12}, respectively. The $5^{12}6^4$ descriptor denotes that the cage is a polyhedron consisting of twelve pentagonal and four hexagonal faces). The interrelation between HS-II and CS-II is similar to that between hexagonal and cubic ices. The analysis of clathrate water frameworks led Jeffrey to conclude that HS-II is theoretically possible. He offers the hydrate $Me_2CHNH_2{\cdot}8H_2O$ as an example of hydrates of this structure (true, it differs markedly from the idealized version).[2] Neither HS-II nor CS-II have been observed in the series with tetraalkylammonium guests.[†] This makes the discovery of the hexagonal structure hydrate with the cation Me_4N^+ as the main guest and the cation Pr_4N^+ as an auxiliary component, where the fluoride ion which is included in a hydrophilic way construct, together with water molecules, a framework, still more interesting.

We have studied the three-component system Me_4NF–Pr_4NF–H_2O and found a tertiary compound $Me_4NF{\cdot}0.5Pr_4NF{\cdot}15H_2O$. Fig. 1 shows a section of the tertiary system Me_4NF–Pr_4NF–H_2O with constant molar ratio of the salts Me_4NF and Pr_4NF 2:1 and variable water content. One can see that the compound formed has a wide range of existence with respect to the mole fraction of water and melts congruently at 21.7 °C. The analysis of the crystals verified the composition of the hydrate $1.02(2)Me_4NF{\cdot}0.5Pr_4NF{\cdot}15.05(5)H_2O$ (the standard deviations for four measurements are given in parentheses).

Single crystals of the hydrate $Me_4NF{\cdot}0.5Pr_4NF{\cdot}15H_2O$ for X-ray experiments and a study of the composition were grown from an aqueous solution which contained 4.6% mol Me_4NF and 2.3% mol Pr_4NF at 5 °C. The water content was determined by a Karl Fisher technique, and Pr_4NF and Me_4NF contents were determined by titration with sodium tetraphenylborate in the presence of a cation-selective electrode.[4] The X-ray structural analysis of a single crystal of this hydrate showed that its cell is hexagonal with parameters $a = 12.290(5)$ A, $c = 59.354(9)$ A (−20 °C), *i.e.* it is a superstructure HS-II with the parameter c increased three-fold. The tertiary compound $Me_4NF{\cdot}0.5Pr_4NF{\cdot}15H_2O$ found is a double clathrate hydrate in which the large H-cavities are occupied by the cations Me_4N^+, while the cations Pr_4N^+ occupy the four-section D_4-cavities which consist of four pentagonal dodecahedra arranged tetrahedrally (Fig.2). The nitrogen atom of the cation Pr_4N^+ substitutes for the water molecule shared by these four cavities, and propyl fragments fill the pentagonal dodecahedra. The fluoride anions substitute for the water molecules, forming the water–anion framework.

Mootz and Seidel showed that the cation Me_4N^+ can be accommodated in one of the big cavities (the volume of the P-cavity is *ca.* 260 Å^3).[5] They found the hydrate $Me_4NOH{\cdot}7.5H_2O$ with the cations Me_4N^+ in the P-cavities ($5^{12}6^3$) and the vacant cavities 4^25^8 (the ratio of the number of small cavities to that of large cavities is 1:2). It can even stabilize a cavity of somewhat larger volume, $4^15^{10}6^6$ (volume *ca.* 290 Å^3) in the hydrate $Me_4NOH{\cdot}10H_2O$ but in this case an orthorhombic structure with few vacant small cavities 4^35^6 (the ratio of the number of small cavities to that of big cavities is 1:1) is observed. However, the cation Me_4N^+ cannot stabilize the structures CS-II and HS-II,[5] being accommodated in the H-cavity $5^{12}6^4$ (volume *ca.* 290 Å^3) where there are many vacant pentagonal dodecahedra (the ratio of the number of small to that of large cavities is 2:1). In this case it might be expected that the hydrate $Me_4NOH{\cdot}16H_2O$ would form. However, if in HS-II not only are the large cavities occupied by the cations Me_4N^+, but the small cavities are also filled with the cations Pr_4N^+, the hydrate turns out to be stable. The calculated density of the double hydrate is 1.194 g cm^{-3} and the packing coefficient ($k = 0.659$) is the largest among clathrates with light guests.

Occupation of the small cavities by an additional component makes the clathrate hydrate more stable which shows up in the increase of the double hydrate melting point compared with that of a common hydrate (without additional component) with the guest of the same kind. In the case of the hydrate $THF{\cdot}H_2S{\cdot}17H_2O$ this increase can be as high as 16.4 °C, even when the filling degree of the small cavities is close to 50%.[6] Pr_4NF, as an additional component, stabilizes

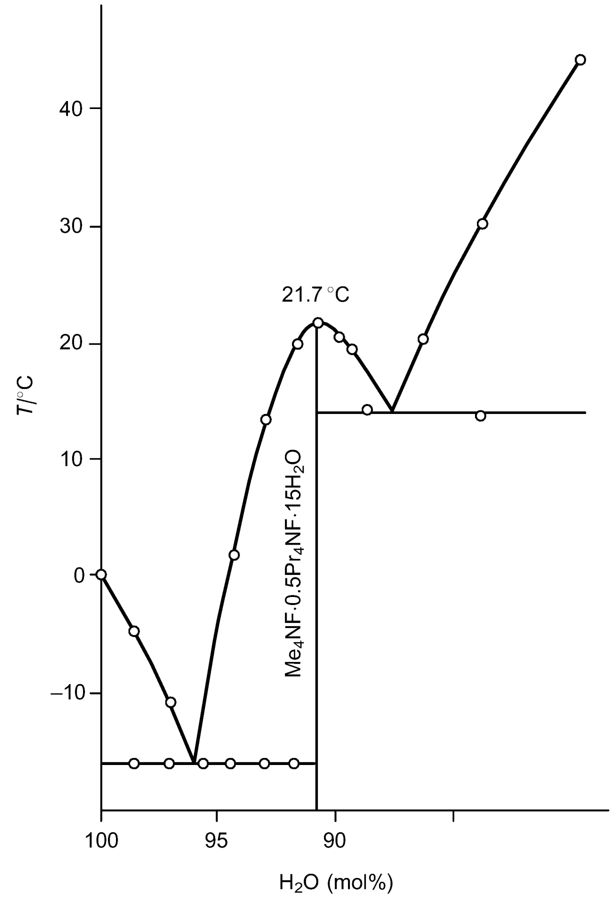

Fig. 1 Section of the phase diagram of the tertiary system Me_4NF–Pr_4NF–H_2O with a constant molar ratio of the salts Me_4NF:Pr_4NF = 2:1 and variable water content.

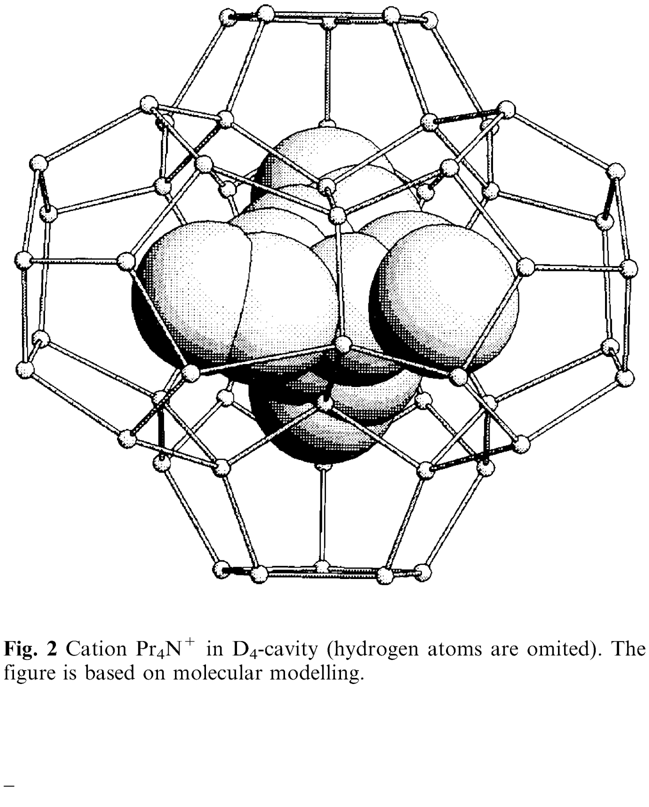

Fig. 2 Cation Pr_4N^+ in D_4-cavity (hydrogen atoms are omited). The figure is based on molecular modelling.

[†] We showed that CS-II double clathrate hydrates with Pr_4NF as an auxiliary component can form.[3]

the clathrate hydrate to a lesser degree because some energy is spent on the building of the four-section D_4-cavity.[3] The maximum increase in the melting point (6.6 °C) with Pr_4NF used as an auxiliary component is observed for the hydrate $TMO \cdot 0.5Pr_4NF \cdot 16H_2O$ ($T_{melt} = -2.6\,°C$) (TMO = trimethylene oxide) compared to the hydrate $TMO \cdot 17H_2O$ melting point (−9.2 °C).[3]

The melting point of the double hydrate $Me_4NF \cdot 0.5Pr_4NF \cdot 15H_2O$ is 21.7 °C and is the highest among the studied double hydrates with Pr_4NF as an auxiliary component. In this case the additional stabilization of the double hydrate relative to the common 1:16 hydrate cannot be discussed because in the case of Me_4NF no such hydrate exists. Clearly, there exists no HS-II hydrate with vacant large cavities because this would be thermodynamically unstable.[7] This suggests mutual stabilization of the clathrate framework by the molecules of the main and auxiliary components.

In conclusion, it should be stated that this is the first known case of the formation of a double clathrate hydrate HS-II with peralkylammonium salts as both the main and an auxiliary component.

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